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High molecular elastomer mouldings - have glass transition at controlled by amts. of isocyanate, polyol and chain extender added

Patent Assignee: MD KASEI KK (MDKA-N); MITSUBISHI HEAVY IND CO LTD (MITO )

Number of Countries: 001 Number of Patents: 002

Patent Family:

Patent No	Kind	Date	Applicat No	Kind	Date	Week
JP 61293214	A	19861224	JP 85134338	A	19850621	198706 B
JP 94096629	B2	19941130	JP 85134338	A	19850621	199501

Priority Applications (No Type Date): JP 85134338 A 19850621; JP 8941805 A 19850620

Patent Details:

Patent No	Kind	Lan	Pg	Main IPC	Filing Notes
JP 61293214	A		7		
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Abstract (Basic): JP 61293214 A

Use of high molecular elastomer mouldings comprises transforming the mouldings at glass transition temp. (Tg) moulding temp. of the elastomer, cooling the transformed mouldings to Tg or less to keep the transformation and heating the transformed mouldings to Tg - the moulding temp. to restore the mouldings to its original form at the time of use.

High molecular elastomer moulding is produced from isocyanate, polyol and chain-extending agent so that Tg of the elastomer comes at about normal temp..

USE/ADVANTAGE - The object is to control Tg of high molecular elastomer to desired temp. by changing kind of isocyanate, polyol or chain-extending agent or rate of the raw materials compounded and to use the elastomer by utilising change of the properties at about Tg.

In an example, isophorone diisocyanate and polyol ''BPE-100'' (by SANN) were compounded so that molar ratio of NCO/OH became 0.82 and reacted to produce prepolymer. To the prepolymer, TDI adduct of timethylolpropane was compounded so that molar of the adduct/the prepolymer became 12. The mixt. was reacted under vacuum as stirring, poured into a mould and cured at 80 deg.C for a day to obtain

polyurethane elastomer mouldings (a) ( $T_g = 50$  deg.C). The mouldings (a) was digested in warm water of 50 deg.C and transformed into the form to cover the arm. The mouldings was left as it was at room temp. (35 deg.C or less) to fix it tightly. The mouldings were heated to at least  $T_g$  by a hair dryer to restore to the original form.

0/4

Title Terms: HIGH; MOLECULAR; ELASTOMER; MOULD; GLASS; TRANSITION; CONTROL; AMOUNT; ISOCYANATE; POLY; OL; CHAIN; EXTEND; ADD

Derwent Class: A25

International Patent Class (Main): C08G-018/08

International Patent Class (Additional): C08J-003/00

File Segment: CPI

PTO 03-86

Japanese Patent  
Document No. 61-293214

POLYMER ELASTOMER MOLDED PRODUCT AND METHOD FOR USING IT  
[Kobunshi Erasutoma Seikeitai Oyobi Sono Shiyo Hoho]

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UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. September 2002

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Applicants : Mitsubishi Heavy Industries Corp.  
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Foreign Language Title : Kobunshi Erasutoma Seikeitai Oyobi  
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English Title : POLYMER ELASTOMER MOLDED PRODUCT  
AND METHOD FOR USING IT

## Specification

### 1. Title of the invention

Polymer elastomer molded product and method for using it

### 2. Patent Claims

1. A method for using a polymer elastomer molded product wherein a deformation force is impressed on a polymer elastomer molded product at a temperature equal to or higher than its glass transition point and lower than its molding temperature, wherein the aforementioned deformation is fixed by cooling said polymer elastomer molded product at a temperature equal to or lower than its glass transition point, and wherein the original shape of said polymer elastomer molded product is restored at the time of its use by heating it at a temperature equal to or higher than its glass transition point and lower than its molding temperature.

2. A polymer elastomer molded product obtained by means of urethane elastomer synthesis from an isocyanate, a polyol, and a chain extending agent by designating the glass transition point in the vicinity of room temperature.

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<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

### 3. Detailed explanation of the invention

(Industrial application fields)

The present invention concerns a polymer elastomer molded product and a method for using it, and more specifically, it concerns a polymer elastomer the glass transition point of which has been designated in the vicinity of room temperature as well as a method for using a polymer elastomer molded product by taking advantage of the drastic changes of its physical properties beneath and above its glass transition point.

(Prior art)

It is known that polymer elastomers are each characterized by the existence of a glass transition point (hereafter abbreviated as "Tg") at which their physical properties (e.g., vertical elastic coefficient, etc.) come to vary by several to several hundred times, and as far as mechanisms used commonly for avoiding the variations of physical properties in the vicinity of the Tg within the operative temperature region are concerned, shoe bottoms, power transmission belts, tires, etc. which, in cases where their Tg values are designated by at extremely low temperatures of approximately -40°C, exhibit low-elasticity attributes even at low temperatures, which are characteristic of ordinary natural rubbers or synthetic rubbers, have been known as application products, and artificial wooden materials, eating utensils, etc. which, based on the designations of their Tg

values at extremely high temperatures of approximately 10[0] ~ 110°C, exhibit such attributes as high elasticity, abrasion, resistance, etc. even at high temperatures have also been known.

(Problems to be solved by the invention)

Incidentally, as far as the glass transition points and physical properties of polymer urethane elastomers are concerned, it is

/2

known that the corresponding parameters of urethane elastomer can be freely designated by optimizing the types of constituent isocyanates, types of polyols, types of chain extending agents, their mixing ratios, presence or absence of annealing, etc. The present inventors then compiled research on the development of a utility method which, based on a mechanism which is unprecedented in the prior art, namely the designation of the Tg of a polymer elastomer in the vicinity of a normal operative temperature, takes advantage of the variations of its physical properties underneath and above the aforementioned temperature, as a result of which the present invention has become completed.

(Mechanism for solving the problems)

The present invention concerns a utility method wherein a minor external deformation force is impressed on a polymer urethane elastomer at a temperature lower than its molding

temperature and equal to or higher than its glass transition point by taking advantage of its peculiar physical property, namely low elasticity, and wherein the deformation of said polymer elastomer is then fixed by means of cooling at a temperature lower than the glass transition point for enabling the use of its resultant physical property, namely high elasticity.

In other words, the present invention concerns a polymer elastomer molded product synthesized by the prepolymer method from an isocyanate, a polyol, and a chain extending agent by designating the glass transition point in the vicinity of room temperature as well as a method for using a polymer elastomer molded product wherein a deformation force is impressed at the aforementioned temperature equal to or higher than its glass transition point and lower than its molding temperature, wherein said deformation is fixed by means of cooling at a temperature lower than its glass transition point, and wherein the original shape of said polymer elastomer molded product is restored at the time of its use by heating it at a temperature equal to or higher than its glass transition point and lower than its molding temperature.

As far as the present invention is concerned, a polymer elastomer molded product is initially formed in a shape necessary for an actual use, and after it has subsequently been induced to deform at a temperature equal to or higher than the glass



transition point of said polymer elastomer and lower than its molding temperature, its deformation is fixed by means of cooling at a temperature lower than the aforementioned glass transition point, as a result of which such attributes of the polymer elastomer as its high elasticity, abrasion resistance, etc. become accessible within a temperature range lower than the glass transition point, whereas, in a case where it becomes heated once again at or above the glass transition point, its deformation automatically becomes cancelled, as a result of which the initial molded shape (or shape analogous to it) becomes restored, and furthermore, the low elasticity attribute of the elastomer becomes accessible within a temperature range higher than the glass transition point. Thus, various applications become conceivable within fields in which morphological variations are functionally required with regard to molded products which exhibit peculiarly different physical properties within its operative temperature region as well as methods for using them.

Any conceivable substances can be employed as the polymer elastomer that constitutes the molded product of the present invention so long as their Tg values coincide with the vicinity of the objective designation temperature, although elastomers which exhibit drastic elasticity variations beneath and above said Tg values are desirable, and as such, a polyurethane elastomer, styrene-butadiene elastomer, nitrile-butadiene elastomer, etc. are normally used.

Next, examples for manufacturing polyurethane elastomers endowed with various Tg values will be explained. There are no special restrictions on the isocyanate component to be used for manufacturing the polyurethane elastomer so long as it is selected from among those which are used commonly for polyurethanes, and it may, for example, be instantiated by diphenylmethane diisocyanate, 2,4- or 2,6-toluylene diisocyanate, - or p-phenylene diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, their crude forms, and their mixtures.

Ones which possess at least two intramolecular hydroxyl groups, furthermore, are used as polyol components, and applicable ones may, for example, be instantiated by polyoxyalkylene polyols which are manufactured by adding alkylene oxides to initialization agents such as polyvalent alcohols (e.g., diols, triols, etc.), aliphatic amines, aromatic amines, etc.; polyester polyols which are manufactured by condensing acids and alcohols; polytetramethylene glycol; polybutadiene polyols; etc.

Chain extending agents or cross-linking agents are instantiated by glycols such as ethylene glycol, butane diol, diethylene glycol, etc., amines such as diethanolamine, triethanolamine, toluylenediamine, hexamethylenediamine, etc., polyisocyanates such as a TDI (toluylene diisocyanate) adduct of trimethylolpropane, triphenylmethane triisocyanate, etc.

If necessary, furthermore, catalysts may also be used for the purpose of accelerating the reaction.

Such catalysts are instantiated by tertiary amines such as triethylamine, tetramethylpropylenediamine, tetramethylhexamethylenediamine, toluylenediamine, etc. and metal catalysts which are represented by such tin-containing catalysts as stannous octoate, stannous oate, dibutyltin dilaurate, etc., and they may each be used alone or as mixtures.

A urethane elastomer is synthesized by using the aforementioned isocyanate, polyol, and chain extending agent as well as, if necessary, the catalyst(s) based on the prepolymer method.

Next, the method for synthesizing the urethane elastomer based on the prepolymer method will be explained.

First, the diisocyanate and polyol are mutually reacted at a specified mixing ratio ( $A = [\text{NCD}]/[\text{OH}]$  molar ratio), as a result of which a prepolymer becomes synthesized. After the reaction has become completed, the chain extending agent is added in such a way that a desired mixing ratio ( $B = [\text{chain extending agent}]/[\text{prepolymer}]$  molar ratio) will become achieved, and after the obtained mixture has subsequently been flowed into a defoaming mold, it is subjected to a cross-linking reaction for 1 or 2 days at a temperature of 60°C within a thermostat dryer, as

a result of which a urethane elastomer becomes synthesized. The foregoing synthesizing operation may be carried out either in a solvent-containing system or solvent-free system.

The following are conceivable as factors which affect the Tg and other physical properties: 1): Types of isocyanates; 2): Types of polyols; 3): Types of chain extending agents; 4): Mixing ratio A; 5): Mixing ratio B; 6): Annealing; etc. A urethane elastomer endowed with a desired Tg profile can be freely synthesized by manipulating these factors 1) through 6).

In the following, an actual embodiment in which the present inventors proceeded to prepare a urethane elastomer to be used in the present invention will be explained, although it goes without saying that it is not binding.

#### Embodiment

A prepolymer was synthesized by reacting 2,4-TDI (trademark: TDI 100, manufactured by Mitsubishi Kasei Corp.) as an isocyanate component together with a polyol (trademark: PP-10000, manufactured by Sanyo Kasei Co.) at a mixing ratio A (NCO/OH molar ratio) of 3.06 in a catalyst-free system. After the reaction had been completed, 1,4-butane diol was added as a chain extending agent in such a way that a mixing ratio B (OH/NCO (prepolymer) molar ratio) of 0.62 would be achieved, and the contents were agitated and reacted in a vacuum. After the obtained product had subsequently been flowed into a mold, it was

cured at a temperature of [6]0°C over a 1-day period, as a result of which a molded product was obtained. The Tg value of said melting point was -5 ~ 0°C (Embodiment Nos. 2 ~ 4).

The respective Tg values of polyurethane elastomers synthesized by redesignating the compositions and mixing ratios according to otherwise identical procedures are summarized in Tables I and II.

Table I

/4

Example No.	Prepolymer	A = [NCO] /[OH]	Chain extending agent	B = [Chain extending agent] /[pre- polymer]	Tg, °C*6
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	(A)	(B)				
1-1	(C)	BPX- S5*1	0.62	(F)	6	51
1-2	(D)	(D)	0.62	(D)	18	107
1-3	(E)	P15- 20*2	0.77	(D)	6	6
1-4	(D)	(D)	0.77	(D)	12	15
1-5	(F)	EPR- 100*3	0.82	(D)	12	48
1-6	(C)	(D)	0.82	(D)	18	92
1-7	(E)	BPX- 38*4	0.82	(D)	12	60
1-8	(D)	(D)	0.82	(D)	18	~ 122

[(A): Isocyanate; (B): Polyol; (C): Isophorone diisocyanate; (D): Same as above; (E): Isophorone diisocyanate/diphenylmethane diisocyanate = 1/1; (F): TDI adduct of trimethylolpropane; (\*1): Polyol manufactured by Asahi Denka Kogyo Co.; (\*2): Polyol manufactured by Asahi Denka Kogyo Co.; (\*3): Polyol manufactured by Sanyo Kasei Kogyo Co.; (\*4): Polyol manufactured by Asahi Denka Kogyo Co.; (\*5): Reaction induced in a 50% solution of 4-methyl-2-pentanone; (\*6): Measurement rendered by using a DSC (differential scanning calorimeter) (average value)]

Table II

Example No.	Prepolymer	A = [NCO] /[OH]	Chain extending agent	B = [Chain extending agent] /[pre- polymer]	Tg, °C <sup>*2</sup>
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	(A)	(B)				
2-1	(C)	P = 1000 <sup>*1</sup>	3	(E)	0.6	-5
2-2	(D)	P = 1000	4	(D)	0.6	5
2-3	(D)	P = 1000	5.2	(D)	0.6	20
2-4	(D)	PP=100 0 <sup>*3</sup>	3.06	(D)	0.62	-5 ~ 0

[(A): Isocyanate; (B): Polyol; (C): 2,4-toluylene diisocyanate;  
(D): Same as above; (E): 1,4-butane diol; (\*1): Polyol  
manufactured by Asahi Denka Kogyo Co.; (\*2): Measurement rendered  
by using a DSC (average value); (\*3): Polyol manufactured by  
Sanyo Kasei Kogyo Co.]

As Tables I and II clearly indicate, it becomes possible to

/5

select the T<sub>g</sub> value freely based on the combination of the hard  
segment of the polyurethane elastomer (i.e., isocyanate and chain  
extending agent) and its soft segment (i.e., polyol). Likewise,  
the respective T<sub>g</sub> values of the styrene-butadiene elastomer and  
nitrile-butadiene elastomer can also be selected freely by  
varying the ratios of their hard segments (i.e., styrene or  
nitrile) and soft segments (i.e., butadiene).

Next, methods for using the polymer elastomer obtained  
according to the aforementioned procedures will be concretely  
shown.

The temperature at which the polymer elastomer is induced to  
become deformed is equal to or higher than the glass transition  
point of said polymer elastomer and below its molding  
temperature. In a case where it is lower than the glass  
transition point, the deformation becomes instantaneously  
recovered [sic], whereas, in a case where it is equal to or

higher than the molding temperature, a new shape becomes conferred on the molded product.

There are no special restrictions on methods for inducing the deformation, and the molded product may, for example, be induced to deform by using a proper tool or bare hands while it abides within an atmosphere the temperature of which is equal to or higher than the glass transition point (e.g., hot air, hot liquid, steam, etc.).

The resulting deformation can be fixed by means of cooling by simply lowering the temperature below the glass transition point immediately after the deformation, although it is also possible to induce a creep deformation at a temperature lower than the glass transition point.

It is possible to cancel the deformation of the molded product of the present invention and to induce specified variations of its morphological or physical properties by simply heating the molded product at a temperature lower than the molding temperature, as a result of which the deformation becomes automatically cancelled while the original shape is being restored, and physical properties peculiar to an elastomer become concomitantly exhibited.

The time required for the restoration of the original shape can, furthermore, be abbreviated by increasing the caloric capacity of heat per unit time or by simply elevating the temperature.



(Application examples)

#### Application Example 1

A method for using the molded product of the present invention will be explained with reference to Figure 1, which shows a plaster cast.

First, the molded product (1), which consisted of the polyurethane elastomer shown in the "1-5" row of Table I the  $T_g$  value of which was designated at  $48^{\circ}\text{C}$  (molding stage of (a) in Figure 1), was immersed in a  $30^{\circ}\text{C}$  warm water, and subsequently, it was induced to deform according to the illustration of (b) in Figure 1, as a result of which the state of (1') became achieved (thermal deformation and cooling fixation stages). An extremely minuscule impression force suffices for inducing the deformation, and therefore, a contiguous retention shape (arm portion (2) in the same figure) can be easily achieved. After the goal of contiguation has been achieved, the deformed shape is retained and left unattended at room temperature ( $35^{\circ}\text{C}$  or lower), as a result of which the molded product (1') becomes cooled, and its contiguously formed shape becomes fixed. After this fixation stage, the vertical elastic coefficient of the obtained molded sheet at a temperature equal to or lower than the  $T_g$  is sufficiently higher than its vertical elastic coefficient above the  $T_g$ , due to which a high elasticity is achieved, and the corresponding portion remains securely fixed without being easily

deformed.

In a case where a plaster cast formed by said molded sheet is released, furthermore, the plaster cast is heated with a hair dryer, etc., and upon the achievement of a temperature equal to or higher than the  $T_g$ , the elasticity of the molded sheet becomes lowered while the molded shape (1) becomes concomitantly restored (heating and deformation cancellation stage (c) of Figure 1), as a result of which the molded sheet (1) can be easily released in a repeatedly re-usable state.

#### Application Example 2

The work fixation material (3) characterized by the structural manifestations shown in (a) ~ (c) of Figure 2 was prepared by using a molded product of the urethane elastomer shown in the "1-7" row of Table I the  $T_g$  value of which was designated at 68°C, which coincides with the vicinity of a normal operative temperature.

Figure 2 (a) shows the shape prevailing at the molding stage, where the molding shape coincides with an actual utility shape.

Next, it is heated at a temperature equal to or higher than the glass transition point, as a result of which the heated structure becomes induced to deform into the desired shape (3') convenient for its storage, transportation, etc., and it is then cooled and fixed [(b) in Figure 2]. It is heated once again at

the time of its use, as a result of which the utility shape manifest at the molding becomes restored.

### Application Example 3

The eating utensil (4) shown in Figures 3 (a) and (b) was prepared by using the urethane elastomer shown in the "1-6" column of Table I the Tg value of which was designated at 92°C, which coincides with a normal operative temperature. Figure 3 (a) shows the molded and/or utility shape, whereas Figure 3 (b) shows the non-utility shape (4'), which has been obtained by thermally deforming and then cooling the former for fixing its deformed shape.

In a case where it is heated once again for canceling its deformation, the shape of (4) shown in Figure 3 (a) becomes restored. /6

Such an eating utensil is advantageous in the sense that its storage space can be conserved during its non-use.

Incidentally, Figure 4 shows an example of the temperature (°C)-vertical elastic coefficient (E) curve of the polymer elastomer of the present invention. It shows the relationships among the Tg, desirable temperature range for inducing deformation, and the molding temperature T<sub>3</sub>.

(Effects of the invention)

As far as the polymer elastomer molded product of the present invention and its utility method are concerned, the  $T_g$  value is designated in the vicinity of a normal operative temperature rather than at an extremely low or extremely high temperature, as in the prior art, based on which it becomes possible to take advantage of the drastic variations of the physical properties of the polymer elastomer molded product underneath and above the  $T_g$  value, and accordingly, it can be used advantageously within fields which functionally require the variations of its physical properties within its operative temperature region.

#### 4. Brief explanation of the figures

Figures 1 (a) ~ (c), Figures 2 (a) ~ (c), and Figures 3 (a) and (b) are each diagrams provided for explaining application embodiments of the present invention.

Figures 1 (a) ~ (c) instantiates a plaster cast, where Figure 1 (a) shows the molding stage, whereas Figure 1 (b) shows the thermal deformation and cooling fixation stages, whereas Figure 1 (c) shows the thermal deformation cancellation stage.

Figures 2 (a) ~ (c) instantiates a work fixation material, where Figure 2 (a) shows the shape at the molding stage, whereas Figure 2 (b) shows the shape at the time of storage and transportation, whereas Figure 2 (c) shows the shape at the time of its use.

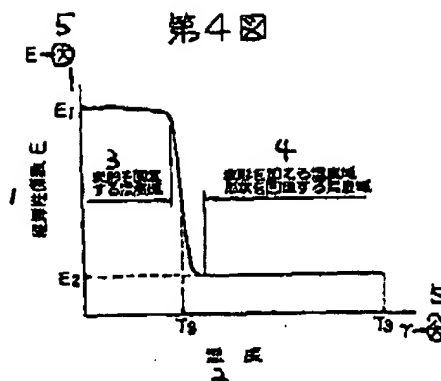
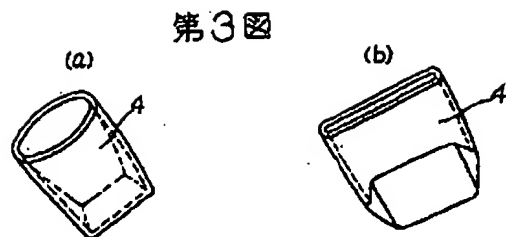
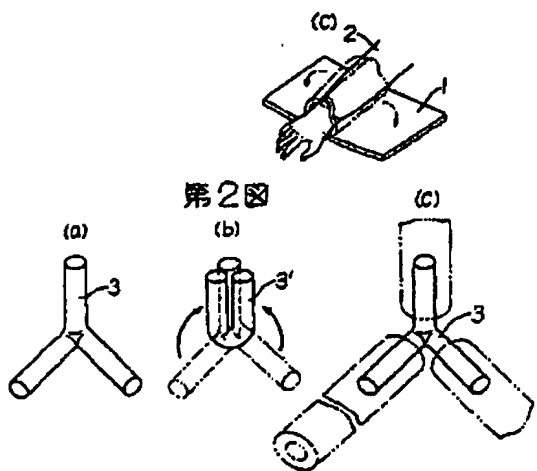
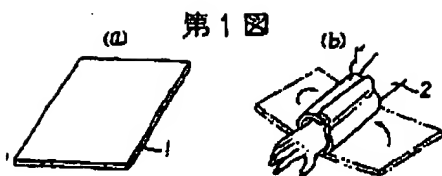
Figures 3 (a) and (b) instantiate an eating utensil, where Figure 3 (a) shows the molded and/or utility shape, whereas Figure 3 (b) shows its shape at the time of its non-use.

Figure 4 is a graph which shows the relationships among the temperature-vertical elastic coefficient (E) curve of the polymer elastomer of the present invention, its glass transition point ( $T_g$ ), and its molding temperature ( $T_3$ ).

Subrepresentative: Akira Uchida

Subrepresentative: Ryoichi Hagiwara

Subrepresentative: Atsuo Anzai



[(1): Vertical elastic coefficient; (2): Temperature; (3): Temperature range over which the deformation is fixed; (4): Temperature range over which the deformation is induced or temperature range over which the initial shape is restored; (5): Higher]

Procedural Amendment Report

/7

December 26, Sho 60[1985]

Dear Judge Michiro Uga, Chief of the Patent Agency:

1. Display of the case

Patent Application No. Tokugan Sho 60[1985]-154598

2. Title of the invention

Polymer elastomer molded product and method for using it

3. Amending party

Relation to the case: Patent Applicant

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Name: (?179): Akira Uchida, patent attorney (and one other)

[Official seal, "Akira Uchida,

Patent attorney"]

5. Date of amendment order: Spontaneous amendment

6. Number of inventions added as a result of the amendment: None

(60.12.2)

[Scratched stamp, "Patent Agency,

60.8.26 ..."]

#### 7. Objects of amendments

(1): "Detailed explanation of the invention" section of the specification

#### 8. Contents of amendments

(1): "Stannous oate" in lines 7 ~ 8 of page 7 of the specification is amended as "stannous oleate."

(2): "PP-10000" in line 19 of page 8 of the same is amended as "PP-1000."

(3): "EPE-100" in the "polyol" row corresponding to Example No. 1-5 in Table I of page 10 of the same is amended as "BPE-100."

(4): "P = 1000" In the "polyol" rows corresponding to Example Nos. 2-1, 2-2, and 2-5 in Table II of page 11 of the same is amended as "P-1000."



## ⑫ 公開特許公報(A)

昭61-293214

⑤ Int. Cl. <sup>4</sup>	識別記号	庁内整理番号	④ 公開	昭和61年(1986)12月24日
C 08 G 18/08	CHQ	7019-4J		
18/00	CHQ	7019-4J		
C 08 J 3/00	CF F	8115-4F	審査請求	未請求 発明の数 2 (全7頁)

⑭ 発明の名称 高分子エラストマー成形体及びその使用方法

⑰ 特 願 昭60-134338

⑱ 出 願 昭60(1985)6月21日

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## 明 細 書

## 1. 発明の名称

高分子エラストマー成形体及びその使用方法

## 2. 特許請求の範囲

## (1) 高分子エラストマー成形体にガラス転移点

以上成形温度未満の温度にて変形を加え、次いで該高分子エラストマーのガラス転移点以下の温度に冷却して上記変形を固定し、使用に際し該高分子エラストマーのガラス転移点以上成形温度未満に加熱して再び元の形状に回復させることを特徴とする高分子エラストマー成形体の使用方法。

## (2) ガラス転移点を室温付近に設定して、イソ

シアネート、ポリオール及び鎖延長剤をプレポリマー法にてウレタンエラストマー合成してなる高分子エラストマー成形体。

## 3. 発明の詳細な説明

## (産業上の利用分野)

本発明は高分子エラストマー成形体及びその

使用方法に関するものであり、更に詳しくは概略室温付近にそのガラス転移点を設定した高分子エラストマー及び高分子エラストマー成形体のガラス転移点前後における物性の急激な変化を利用した使用方法に関するものである。

## (従来の技術)

高分子エラストマーには縦弾性係数等の物性が数倍～数百倍に変化するガラス転移点温度(以下T<sub>g</sub>と略す)が存在することが知られ、通常使用温度領域にてT<sub>g</sub>前後の物性変化を避ける手段として約-40℃前後の極低温にT<sub>g</sub>を設定して低温時にも通常の天然ゴムや合成ゴムのような低弾性率な特性を生かすようにした靴底、動力伝達ベルト、タイヤ等に利用したり、また約100～110℃の極高温にT<sub>g</sub>を設定して高温時にも高弾性率、耐摩耗等の特性を生かすようにした人工木材、食器等に利用されていた。

## (発明が解決しようとする問題点)

ところで、高分子ウレタンエラストマーのガ

ラス転移点温度及び物性は例えばウレタンエラストマーの場合、構成するイソシアネートの種類、ポリオールの種類、鎖延長剤の種類、配合比、アニーリング等により自由に設定できることが知られている。そこで本発明者らは従来試みられることのなかつた高分子エラストマーの通常使用温度前後に $T_g$ を設定し、上記温度前後での物性変化を利用した使用方法を開発すべく研究した結果、本発明に達したものである。(問題点を解決するための手段)

本発明は高分子ウレタンエラストマーに、その成形温度未満かつガラス転移点以上の温度で低弾性率な物性を利用して小さな外力で変形を加え次いで該高分子エラストマーをガラス転移点温度より低温に冷却することにより変形を固定させ、高弾性率な物性を利用する使用方法に関するものである。

すなわち本発明はガラス転移点の使用温度付近であるよう設定し、イソシアネート、ポリオール及び鎖延長剤をブレポリマー法により合成

を備えた成形体及び使用方法にて形状変化を要するような機能が要求される分野で種々の利用が考えられる。

本発明の成形体を構成する高分子エラストマーとしては、目的とする設定温度の近傍に $T_g$ を有するエラストマーであれば、いかなる物質でもよいが、該 $T_g$ の前後における弾性率変化の大なるエラストマーが好ましく、通常、ポリウレタンエラストマー、ステレン-ブタジエンエラストマー、ニトリル-ブタジエンエラストマー等が用いられる。

次に各種の $T_g$ を有するポリウレタンエラストマーの製造例について説明する。ポリウレタンエラストマーを製造するのに使用されるイソシアネート成分としては、通常ポリウレタンに使用されるものであれば特に制限はなく例えばジフェニルメタンジイソシアネート、2,4-又は、2,6-トリレンジイソシアネート、m-又はp-フェニレンジイソシアネート、イソホロンジイソシアネート、ヘキサメチレンジイソシ

アネート及びこれらの粗成分あるいは混合物が使用される。

またポリオール成分としては、1分子中に少なくとも2個以上の水酸基を有するものが用いられ、例えばジオールやトリオールなどの多価アルコール、脂肪族アミン、芳香族アミン等を開始剤とし、これにアルケンオキサイドを付加して製造されるポリオキシアルケンポリオール、酸とアルコールの縮合により製造されるポリエステルポリオール、あるいはポリテトラメチレングリコール、ポリブタジエンポリオールなどが使用される。

鎖延長剤や架橋剤としては、エチレングリコール、ブタンジオール、ジエチレングリコールなどのグリコール、ジエタノールアミン、トリエタノールアミン、トリレンジアミン、ヘキサメチレンジアミンなどのアミン類、トリメチロールプロパンのTDI(トリレンジイソシアネート)アダクト、トリフェニルメタントリイソシアネートなどのポリイソシアネートなどが挙げ

られる。

また必要に応じて反応を促進する為に触媒が使用される。

触媒としてはトリエチルアミン、テトラメチルプロピレンジアミン、テトラメチルヘキサメチレンジアミン、トリレンジアミンなどの第3級アミン類又はスタナスオクトエート、スタナスオエート、ジブチル錫ジラウレートのような錫系触媒に代表される金属触媒があり、これらはおのおの単独にあるいは混合して使用される。

上記イソシアネート、ポリオール、鎖延長剤、及び必要に応じて触媒を用いてプレポリマー法によりウレタンエラストマーの合成を行う。

次にプレポリマー法によるウレタンエラストマーの合成方法を説明する。

まず、ジイソシアネートとポリオールを特定の配合比  $A = [NCO] / [OH]$  モル比で反応させ、プレポリマーを合成する。反応終了後、希望する配合比  $B = [\text{鎖延長剤}] / [\text{プレポリマー}]$  モル比になるよう鎖延長剤を添加し、そ

の後脱泡し型に流し込み、恒温乾燥器にて温度  $80^{\circ}\text{C}$  で1日から2日間架橋反応を行なわせウレタンエラストマーを合成する。以上の合成は溶媒系非溶媒系のいずれでも可能である。

$T_g$  や物性に及ぼす要因としては1) イソシアネートの種類、2) ポリオールの種類、3) 鎖延長剤の種類、4) 配合比A、5) 配合比B、6) アニリングなどが考えられるが、これら1) から6) の要因を変えることにより希望する  $T_g$  物性をもつウレタンエラストマーを自由に合成することが可能である。

以下本発明で用いられるウレタンエラストマーについて、本発明者らが作成した実例を挙げて説明するが、勿論これに限定されるものではない。

#### 例

イソシアネート成分として2,4-TDI〔三菱化成(株)製、商品名TDI 100〕とポリオールとして三洋化成(株)製、商品名PP-10000を、配合比A ( $NCO/OH$  モル比) 3.06にて無触媒

にて反応させプレポリマーを合成した。反応終了後、鎖延長剤として1,4-ブタンジオールを配合比B ( $OH/NCO$  (プレポリマ) モル比) 0.62となるように加え、真空下攪拌して反応させる。その後型に流し込み温度  $80^{\circ}\text{C}$  にて1日間キュアして成形体を得た。該成形体の  $T_g$  は  $-5 \sim 0^{\circ}\text{C}$  であつた(例42-4)。

組成と配合比を変えて同様に合成したポリウレタンエラストマーとその  $T_g$  を表1及び表2にまとめて示す。

表 1

例 №	プレポリマー		A = [NCO] /[OH]	鎖延長剤	B = [鎖延長剤] /[プレポリマー]	T <sub>g</sub> °C <sup>6)</sup>
	イソシアネート	ポリオール				
1-1	イソフロロンジイソシアネート	BFX-55 <sup>1)</sup>	0.62	トリメチロールプロパ ンのTDIアダクト	6	31
1-2	同上	同上	0.62	同上	18	107
1-3	イソフロロンジイソシアネート/ ジフェニルメタンジイソシアネ ート=1/1	F15-20 <sup>2)</sup>	0.77	同上	6	6
1-4	同上	同上	0.77	同上	12	15
1-5	イソフロロンジイソシアネート	EPB-100 <sup>3)</sup>	0.82	同上	12	48
1-6	同上	同上	0.82	同上	18	92
1-7	イソフロロンジイソシアネート/ ジフェニルメタンジイソシアネ ート=1/1	BFX-33 <sup>4)</sup>	0.82	同上	12	68
1-8	同上	同上	0.82	同上	18	~122

1) 旭電化工業(株)製ポリオール

2) 旭電化工業(株)製ポリオール

3) 三洋化成工業(株)製ポリオール

4) 旭電化工業(株)製ポリオール

5) 4-メチル-2-ペンタノンの50%溶液にて反応

6) DBO(差動型走査熱量計)にて測定(平均値)

表 2

例 №	プレポリマー		A = [NCO] /[OH]	鎖延長剤	B = [鎖延長剤] /[プレポリマー]	T <sub>g</sub> °C <sup>2)</sup>
	イソシアネート	ポリオール				
2-1	2,4-トリレンジイソシ アネート	P=1000 <sup>1)</sup>	3	1,4-ブタンジオール	0.6	-5
2-2	同上	P=1000	4	同上	0.6	5
2-3	同上	P=1000	5.2	同上	0.6	20
2-4	同上	PP-1000 <sup>3)</sup>	3.06	同上	0.62	-5~0

1) 旭電化工業(株)ポリオール

2) DBOにて測定(平均値)

3) 三洋化成工業(株)ポリオール

表1及び表2から明らかなようにポリウレタンエラストマーのハードセグメント(イソシアネート、鎖延長剤)とソフトセグメント(ポリオール)の組み合わせにより自由に $T_g$ を選択することができる。同様にしてスチレン-ブタジエンエラストマー、ニトリル-ブタジエンエラストマーにおいてもハードセグメント(スチレンあるいはニトリル)とソフトセグメント(ブタジエン)の割合を変えることにより、 $T_g$ を自由に選択できる。

次に上記のようにして得られた高分子エラストマー成形体の使用方法を具体的に示す。

本発明の方法における高分子エラストマーに变形を与える温度は該高分子エラストマーのガラス転移点温度〜成形温度未満であるが、ガラス転移点温度以下では变形が即座に回復し、また成形温度以上では成形体に新たな形状を与えることになり好ましくない。

变形の与え方については特に制限はなく、成形体をガラス転移点温度以上の雰囲気(例えば

加熱空气中、加熱液体中、水蒸気中など)に置き、適当な道具もしくは素手で変形を与えることができる。

変形を固定するには、変形を与えた直後にガラス転移点以下の温度に冷却するだけで良いがガラス転移点温度以下でクリープ変形を与えることも可能である。

本発明の成形体から変形を取除き、所定の形状もしくは物性に变化させるにはガラス転移点温度以上、成形温度未満の温度に成形体を加熱すれば良く、変形は自動的に除去され形状が回復すると共に物性もエラストマーとしての物性を示す。

また、形状を回復させるための加熱の時間当り熱量を多くする程、また単に温度を高くする程形状を回復する時間は短くなる。

(実施例)

#### 実施例 1

本発明の成形体の使用方法を第1図のギブスに説明する。

先ず $T_g$ を48℃に設定した表1の1-5に示したポリウレタンエラストマーからなる成形板1〔第1図(a)成形段階〕を50℃の温水に数分浸した後、第1図(b)のように変形を加え1'のようにする(加熱変形・冷却固定段階)。変形を加える力はごくわずかで良いから保持形状(同図中では腕部2)に密着させることは容易である。密着後変形を保持したまま室温(約35℃以下)に放置しておけば、成形板1'は冷却され密着形状にて固定される。固定後 $T_g$ 以下の温度では該成形板の縦弾性係数は $T_g$ 以上の縦弾性係数に比して充分大きく高弾性となるため容易には変形せず該部位はしっかりと固定される。

更に該成形板によるギブスを脱着するときはヘヤードライヤー等でギブスを加熱し、 $T_g$ 以上の温度にすることにより成形板は低弾性になると共に成形時の形状1に回復するため〔第1図(c)加熱、変形解放段階〕容易に脱着できると共に、成形板1は繰り返し使用可能な状態とな

る。

#### 実施例 2

通常使用温度前後の68℃に $T_g$ を設定した表1の1-7に示したウレタンエラストマーの成形体を用いて、第2図(a)〜(c)に示す構造の工作物固定材料3を作成した。

第2図(a)は成形時形状を示し実際の使用形状に成形してある。

次にガラス転移点以上の温度に加熱して、加熱した構造物を保管運搬等に便利な所望形状3'に変形させ冷却固定する〔第2図(b)〕。使用に際しては再度加熱し成形時の使用形状まで回復させる。

#### 実施例 3

通常使用温度前後の92℃に $T_g$ を設定した表1の1-6に示したウレタンエラストマーを用いて第3図(a)及び(b)に示す食器4を作成した。第3図(a)は成形及び使用形状を示し、これを加熱変形したのち冷却して変形を固定したものが第3図(b)に示す未使用時の形状4'である。

再び加熱して変形解放すれば、第3図(a)の4の形状に戻る。

このような食器は未使用時に保管場所が小さくてすむ利点がある。

なお、第4図に本発明における高分子エラストマーの温度(℃)—縦弾性係数(E)曲線の例を示す。 $T_g$ と変形を加えるに好ましい温度域及び成形温度 $T_3$ の関係を示している。

(発明の効果)

本発明の高分子エラストマー成形体及びその使用法は、従来のように $T_g$ を極低温や極高温に設定するのではなく、通常使用温度前後に設定し、 $T_g$ 前後での高分子エラストマー成形体の急激な物性変化を利用することにより、使用温度領域にて異種物性を備えた機能をもつ材料を要する種々の分野において、有利に用いることができる。

#### 4. 図面の簡単な説明

第1図(a)～(c)、第2図(a)～(c)、第3図(a)及び(b)はいずれも本発明の実施態様を説明する図で

ある。

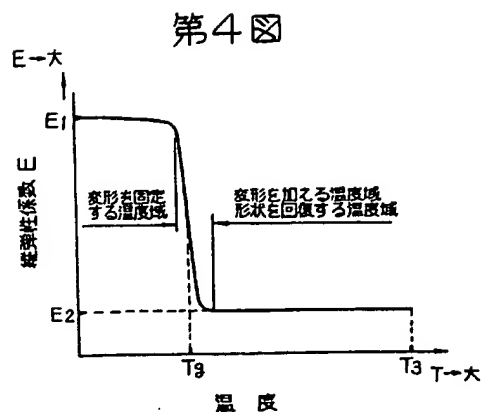
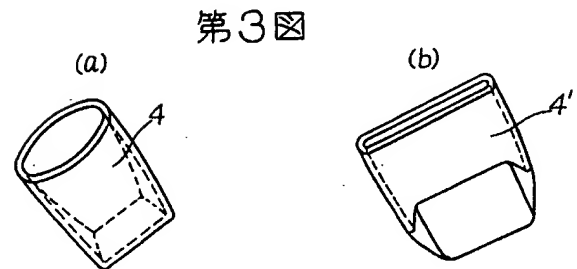
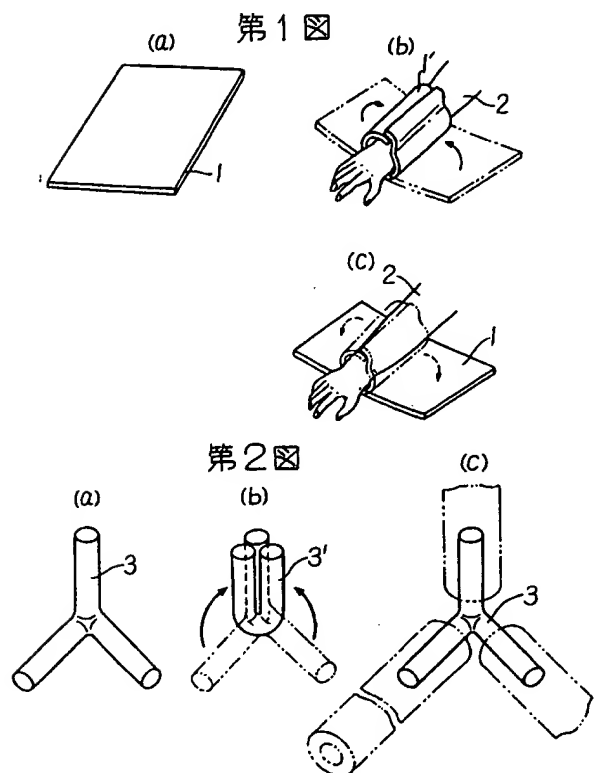
第1図(a)～(c)はギプスであり第1図(a)は成形段階、第1図(b)は加熱変形、冷却固定段階、第1図(c)は加熱変形解放段階を示す。

第2図(a)～(c)は工作物固定材料であり、第2図(a)は成形時形状、第2図(b)は保管運搬時形状、第2図(c)は使用時形状を示す。

第3図(a)及び(b)は食器であつて、第3図(a)は成形時又は使用時形状を第3図(b)は未使用時形状を示す。

第4図は本発明における高分子エラストマーの温度—縦弾性係数(E)曲線と、ガラス転移点温度 $T_g$ 、成形温度 $T_3$ の関係を示すグラフである。

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復代理人	萩 原 亮 一
復代理人	安 西 篤 夫



手 続 補 正 書

昭和 60 年 12 月 26 日

特許庁長官 宇賀 道 郎 殿

1. 事件の表示

昭和 60 年特許願第 134558 号

2. 発明の名称 高分子エラストマー成形体及び  
その使用方法

3. 補正をする者

事件との関係 特許出願人

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(ほか1名)

5. 補正命令の日付 自 発 補 正

6. 補正により増加する発明の数 ナシ

{ 60.12. 2 }



2. 補正の対象

(1) 明細書の「発明の詳細な説明」の欄

3. 補正の内容

(1) 明細書7頁7～8行の「スタナスオエート」を「スタナスオレエート」と訂正する。

(2) 同8頁19行の「PP-10000」を「PP-1000」と訂正する。

(3) 同10頁表1中の例1-5のポリオール欄の「BPE-100」を「BPE-100」と訂正する。

(4) 同11頁表2中の例2-1, 2-2, 2-3のポリオール欄の「P-1000」を各々「P-1000」と訂正する。